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[Title of the Invention]

Process for Lubricating Pretreatment of Galvanized Steel Plates

[Abstract]

[Purpose] To provide a process for lubricating pretreatment to improve press workability, primary rust prevention during a term of storage and detergency for removing a lubricant in galvanized steel plates.

[Constitution] Before applying a press working lubricant on the surface of a galvanized steel plate, an aqueous solution of one or more compounds selected from the group consisting of alkali metal salts, alkaline earth metal salts and ammonium metal salts of silicic acid, boric acid and phosphoric acid is applied on the surface and dried to form a coat of 30-200 mg/m^2 thereon.

[CLAIM]

[Claim 1] A process for lubricating pretreatment of a galvanized steel plate, which comprises, before applying a press working lubricant on the surface of the galuanized steel, applying an aqueous solution of one or more compounds selected from the group consisting of alkali metal salts, alkaline earth metal salts and ammonium salts of silicic acid, boric acid and phosphoric acid on the surface of the plate, followed by drying to form a coat of 30-200 mg/m^2 thereon.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application]

The present invention relates to a process for lubricating pretreatment of galvanized steel plates before applying a press working lubricant on the surface, said galvanized steel plates being widely used in the automobile industry and home electrical products industry as typical manufacturers. By such pretreatment, improvement of press workability, primary rust prevention during a term of storage and improvement of detergency for removing a lubricant are effectively attained.

[0002]

[Prior Art]

As for press working oil for galvanized steel plates,

highly viscous oil containing oil and fat and a sulfur compound in addition to mineral oil or oil and fat or synthetic oil has been used. In general, since the press working is continuously carried out, the temperature of tools is raised up to 50-100°C and processing materials also generate heat due to plastic deformation. The press working in such a state gives rise to a problem that washing and removal of residual oil film after processing is insufficient.

[0003]

In general, press working oil is poor in rust preventive ability, and it is another problem that the press shaped galvanized steel plate easily generates white rust on the surface during storage, particularly red rust in addition to white rust mainly at the plate edge during transit. In addition, in a degrease washing step for chemical conversion coating as pretreatment prior to painting of the plate after press working, press oil film is not removed completely in some cases and white and red rust generate in many cases. In any cases, since poor chemical conversion coating is induced, there is a problem that coating quality considerably decreases.

[0004]

Next, as rust preventive oil for galvanized steel plates, base oil containing an alkylsulfonate salt or carboxylate salt has been used. This oil, however, is poor in lubrication, and so, in order to conduct press working on a galvanized steel

plate on which has been applied such oil, it is necessary to apply further another press working oil on the plate.

[0005]

In another case, multi-functional oil that affords sufficient rust prevention and lubrication by only one application has been used, in which very fine powder of a specific solid lubricant has been added. In this oil, however, there is a problem in long term stability. In addition, pretreatment with a phosphate prior to application of lubricating oil reduces friction between a metal mold and a metal during press working to improve the press working. In this process, however, in addition to the pretreatment, many working steps are required for removal of the phosphate film remaining on the surface after press working. This process is not practical, accordingly. In this situation, it has been desired that a process for pretreatment will be developed for improving lubricity, rust prevention and detergency of lubricants regardless of the type of lubricants.

[0006]

[Problems that the Invention is to Solve]

The present invention was made for the purpose of solving the problems in press working of galvanized steel plates using the so far used lubricating oil. In the invention, it was found that the application of an aqueous solution of an alkali metal or alkaline earth metal or ammonium salt of silicic acid, boric

acid or phosphoric acid on the surface of a galvanized steel plate, followed by drying to form a coat, before the application of a press working lubricant, affords better lubricity (press workability), rust prevention and detergency to the plates than the use of the known lubricating oil. Thus, the invention was completed.

[0007]

[Means for Solving the Problems]

Briefly, the present invention relates to a process for lubricating pretreatment of a galvanized steel plate, which comprise, before applying a press working lubricant on the surface of the plate, applying an aqueous solution of one or more compounds selected from the group consisting of alkali metal salts, alkaline earth metal salts and ammonium salts of silicic acid, boric acid and phosphoric acid on the surface of the plate, followed by drying to form a coat of 30-200 mg/m^2 thereon.

[0008]

In the invention, the coat on the surface of the galvanized steel plate prior to the application of a lubricant may be formed by application of an aqueous solution of one or more of compounds selected from the group consisting of alkali metal salts, alkaline earth metal salts and ammonium salts derived from silicic acid, boric acid and phosphoric acid, followed by drying. In general, though treatment with a

phosphate salt prior to the application of a lubricant is effective in improving lubricity, it has not been employed because of the necessity of multiple steps. In this invention, investigation was made in order to form a rust preventive and lubricating coat on the galvanized surface. As a result, it was found that the application of an aqueous solution of the above-mentioned compound and subsequent immediate drying to form a coat of 30-200 mg/m^2 successively affords a pre-processing agent excellent in lubricity, rust prevention and removal of oil.

[0009]

[Action]

The silicate used in the invention may be represented by a general formula of M_2O, $xSiO_2$, wherein M is an alkali metal or alkaline earth metal and x is a positive integer of 1 to 5. Ammonium salts may also be applied. The borate includes alkali metal salts, alkaline earth metal salts and ammonium salts of HBO_2, H_3BO_3, $H_2B_4O_7$, $H_2B_6O_{12}$, and $H_2B_8O_{13}$. The phosphate includes alkali metal salts, alkaline earth metal salts and ammonium salts of H_3PO_4, HPO_3, $H_4P_2O_6$, HPO_2, H_3PO_2, $H_3P_3O_9$, and polyphosphoric acid, e.g., $H_4P_2O_7$, $H_5P_3O_{18}$, $H_6P_4O_{13}$.

[0010]

In order to form a coat, an aqueous solution of one or more of those compounds is applied and dried. The amount of coating less than 30 mg/m^2 affords no improvement of lubricity

and has no effect as a pre-processing agent. The amount over 200 mg/m^2 improves the lubricity, but rust prevention and removal of oil are decreased. The coating, accordingly, is preferably made at 30-200 mg/m^2.

[0011]

There is no limitation on the concentration and method of coating, though the concentration of the above compound over 5wt% is not preferred because the galvanized surface is corroded and dissolved. At less than 0.02wt%, the prefixed amount of coating is difficult because drying is hardly achieved and the appearance is uneven in many cases. The preferred concentration, accordingly, is in a range of 0.02-5.0wt%, more preferably 0.05-2.0wt%. As a way of coating, a roll coater, air knife coating, and the like may be applied.

[0012]

[Examples]

The following examples will specifically explain the process for lubricating pretreatment of galvanized steel plates in the invention along with Comparative Examples. As a test plate, a commercially available double alloy galvanized steel plate (single plating thickness of 45 g/m^2, plate thickness 0.8 mm) was used, and oil on the surface was completely removed by treatment with trichloroethane. The test plate was then immersed in a pre-processing agent at 80°C for 5 seconds, then pressed with a roll presser, and dried with

a dryer to form a coat. The coating amount was adjusted by adjusting the coating concentration and the pressing amount.

[0013]

As a lubricant after pretreatment, commercially available rust preventive oil was applied to the test material at a rate of 2 g/m^2. Characterization was performed by means of a deep drawing test, Bauden test, rust preventive test, and defat test. The test methods and the criteria are as follows.

[0014]

(1) Lubrication test (deep drawing test)

a. Size of the test plate: 90 mmϕ

b. Die diameter: 42.5 mm

c. Punch diameter: 40.0 mm

d. Shoulder radius of punch and die: 8 mm

e. Drawing rate: 400 mm/min.

f. Wrinkle pressing load: 1000 kgf

g. Assessment: Determined according to the deep drawing rate of the following formula:

$(1 - D/D_0) \times 100\%$

D_0: Diameter of the test piece before testing

D: Diameter of the test piece after testing

Evaluation was made by means of deep drawing rate. O: 15% or more; Δ: 10-15%; ×: less than 10%.

[0015]

(2) Lubrication test (Bauden test)

a. Size of the test plate: 70 mm x 150 mm

b. Pressure contact element: SUJ-2 steel ball 10 mmϕ

c. Load: 1 kg

d. Fold-moving rate: 100 mm/s

e. Fold-moving distance: 20 mm

f. Assessment: Frequency of fold movement until the friction coefficient reaches 0.25

Evaluation was made by means of frequency of fold movement. O: 100 or more; Δ: 20 or more; x: 20 or less.

[0016]

(3) Rust preventive test (wetting stack test)

a. Size of the test plate: 70 mm x 150 mm

b. Temperature: 49 ± 1°

c. Relative temperature: 95% or more

d. Stack force: 70 kgf-cm

e. Time: 240 hours

f. Assessment: The area (%) generating white rust on the test piece

Evaluation was made by means of generation of rust. O: no generation of rust; Δ: less than 20%; x: 20% or more.

(4) Defat test

a. Size of the test plate: 70 mm x 150 mm

b. Preparation of the test piece: Each test piece was applied with a pre-processing agent and a lubricant, stacked under 70 kgf-cm, and allowed to stand in a thermostat and humidistat

test apparatus kept at a temperature of 50°C and a humidity of 95% for 7 days. Thus resulting piece was used as a test material.

c. Oil-removing agent: trade name: Fine Cleaner L4480 [Nihon Parkerizing Co.]

d. Concentration: 18 g/L

e. Temperature: 40°C

f. Time: 3 minutes in a perfectly static bath

g. Assessment: Defat test piece was washed with running water for 30 seconds, and after standing for 30 seconds the wetting area (%) was observed. Evaluation: O: 100% wetting; Δ: 80% or more; ×: less than 80%.

[0018]

Table 1

	No	Preprocessing agent	Coat (mg)	Deep drawing	Bauden property	Rust prevention	Defat
Example	1	K silicate	50	O	O	O	O
	2	Na tetraborate	150	O	O	O	O
	3	Na pyrophosphate	30	Δ	Δ	O	O
	4	Mg silicate	200	O	O	Δ	O
	5	Na metaborate Ammonium monohydrogen phosphate	70 30	O	O	O	O
	6	Ammonium dihydrogen phosphate	50	O	O	O	O
	7	Na metasilicate	70	O	O	O	O
	8	Mg borate K silicate	100 80	O	O	O	O
	9	Ammonium monohydrogen phosphate	200	O	O	Δ	O
	10	Ammonium borate	100	O	O	O	O
	11	2Na phosphate	50	O	O	O	O
	12	K silicate 2Na phosphate	70 80	O	O	O	O
Comperative Example	1	Rust preventive oil alone	0	×	×	O	O
	2	2Na phosphate	20	×	×	O	O
	3	Na tetraborate	10	×	×	O	O
	4	Na metasilicate	300	O	O	×	Δ
	5	Ammonium monohydrogen phosphate	500	O	O	×	Δ
	6	Press oil alone	0	O	O	×	×

[0019]

Table 1 shows the results in 12 Examples and 6 Comparative Examples. In Comparative Example 1, rust preventive oil alone was used. In Comparative Examples 2 and 3, the coating amount is less than 30 mg/m^2, and in Comparative Examples 4 and 5, it is over 200 mg/m^2. In Comparative Example 6, press oil alone was used. As seen from these results, it is clear that the pre-processing agent of the invention is excellent in lubricity, rust prevention and oil-removing property.

[0020]

[Advantage of Invention]

As described above, it becomes possible to improve rust prevention during preservation and lubricity in the press working of the galvanized steel plate used in an automobile industry, etc., when the lubricating pretreatment process of the invention is applied to such a plate. It is not necessary to consider the component of a lubricant that is applied subsequently.